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Rheinheimer et al.

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[54] **ISOXAZOLINES, THEIR PREPARATION AND THEIR USE**

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[52] **U.S. Cl.** **71/94**; 71/88; 546/209; 546/275; 548/240

[58] **Field of Search** 71/88, 94; 546/275, 546/209; 548/240

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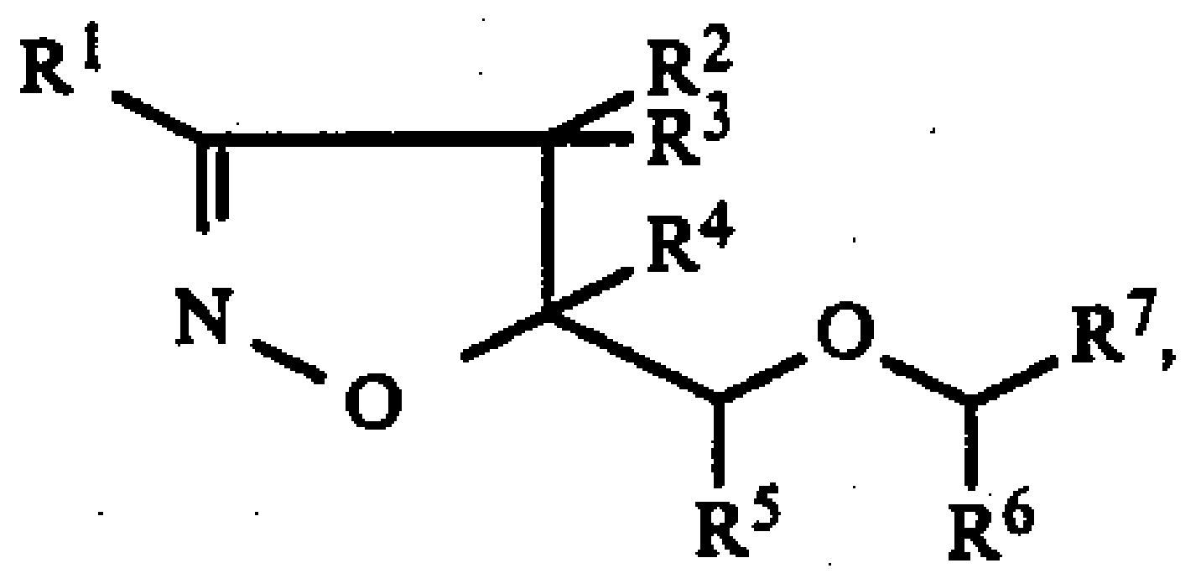
[57] **ABSTRACT**

Isoxazolines of the general formula I



where the substituents have the following meanings:

R^1 is C_1–C_{12}-alkyl, C_3–C_7-cycloalkyl, substituted or unsubstituted phenyl, or a saturated or unsaturated 5- or 6-membered heterocycle;

R^2, R^3, R^4, R^5 and R^6 are hydrogen, C_1–C_4-alkyl or benzyl and

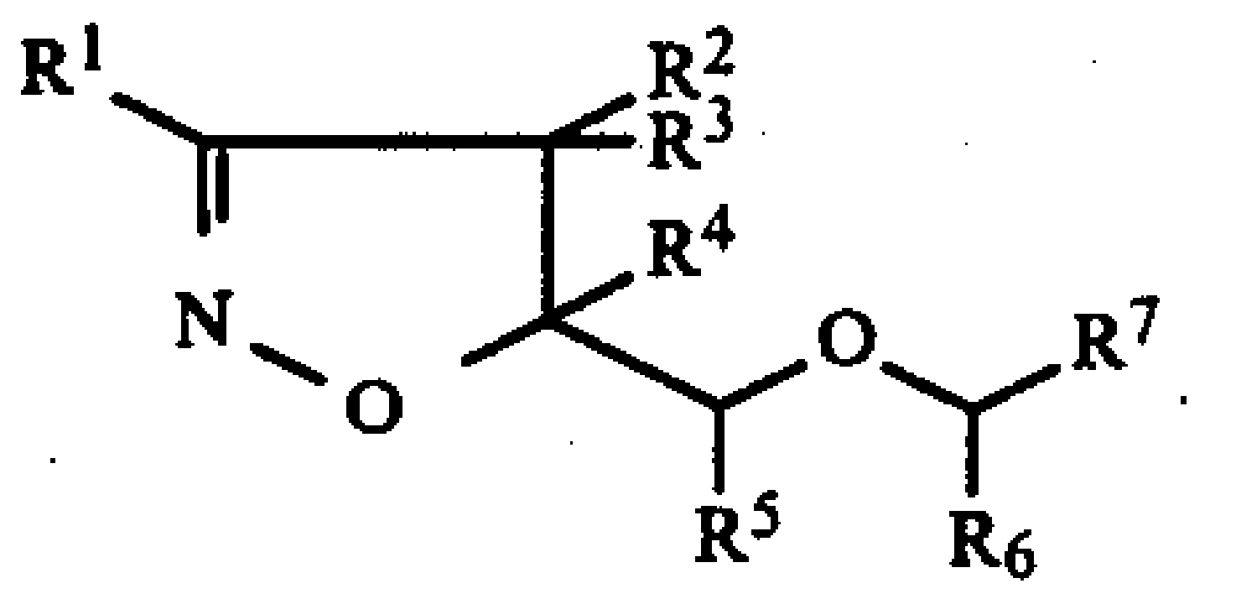
R^7 is substituted or unsubstituted C_2–C_6-alkenyl, C_5–C_7-cycloalkenyl, phenyl, naphthyl or thienyl,

processes for their manufacture, and their use.

3 Claims, No Drawings

ISOXAZOLINES, THEIR PREPARATION AND THEIR USE

The present invention relates to isoxazolines of the general formula I



I

where R^1 is C_1–C_{12}-alkyl, C_3–C_7-cycloalkyl, phenyl which can carry one to five halogen atoms and/or one to three of the groups C_1–C_4-alkyl, C_1–C_4-alkoxy and/or C_1–C_4-haloalkyl, or a saturated or unsaturated 5-membered or 6membered heterocyclic structure containing a nitrogen, oxygen or sulfur atom as a ring member, R^2, R^3, R^4, R^5 and R^6 are each hydrogen, C_1–C_4-alkyl or benzyl and R^7 is C_2–C_6-alkenyl or C_5–C_7-cycloalkenyl, where these groups may carry one to three phenyl radicals and/or halogen atoms, or is phenyl which may carry one to three of the substituents C_1–C_4-alkyl, C_1–C_4-alkoxy, C_1–C_4-haloalkyl, phenyl or phenoxy, cyano and/or halogen, or is naphthyl or thienyl, where these aromatic rings may carry one to three C_1–C_4-alkyl groups and/or halogen atoms.

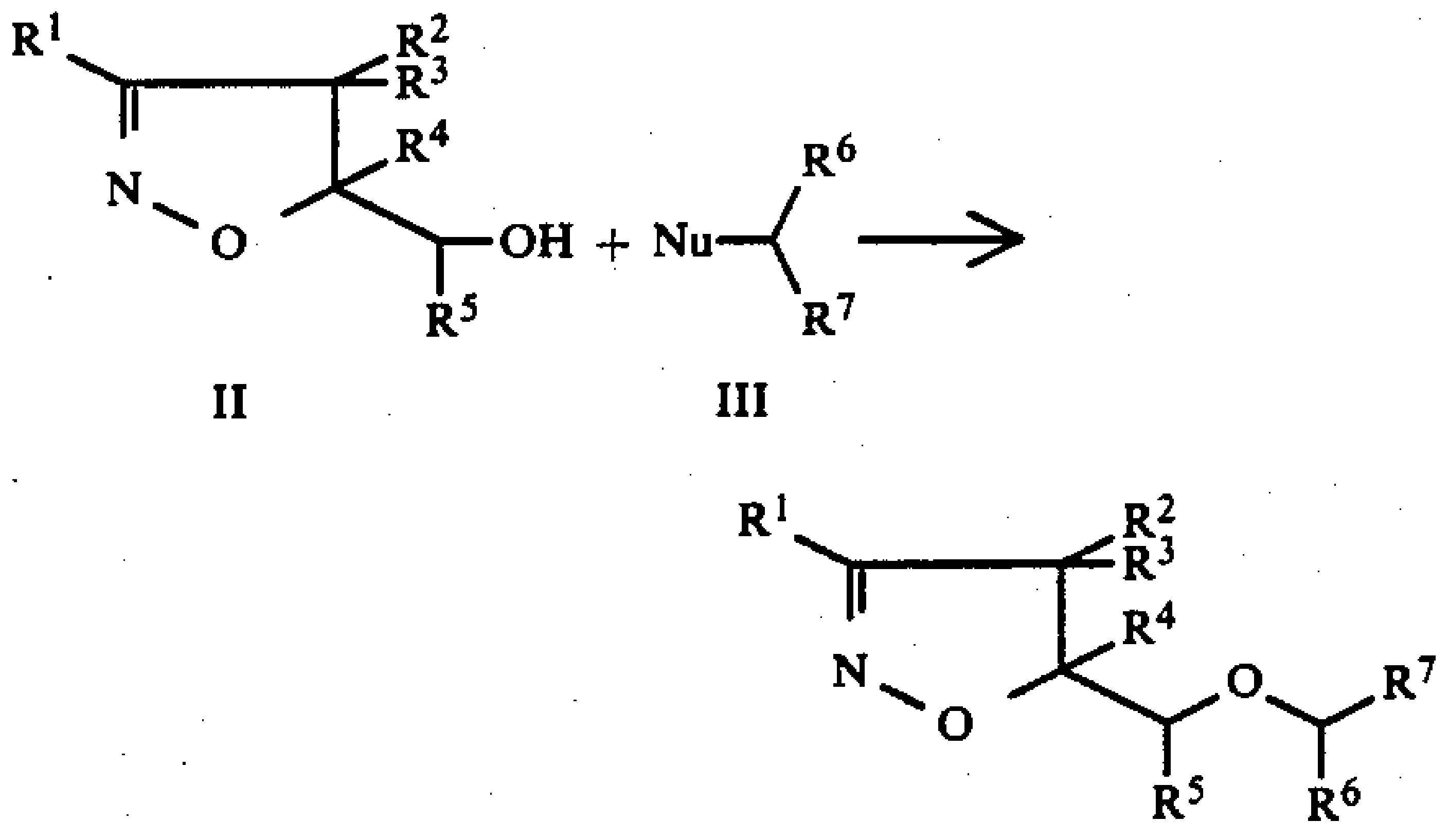
The present invention furthermore relates to processes for the preparation of the compounds I, herbicides which contain these compounds and methods for controlling undesirable plant growth with the compounds I.

DE-A 27 24 677 describes herbicidal 2-(benzyloxymethyl)-tetrahydrofurans. However, because of the poor selectivity with respect to weeds and the relatively high application rates, their action is unsatisfactory.

It is an object of the present invention to provide compounds having improved herbicidal properties.

We have found that this object is achieved by the isoxazolines I defined at the outset. We have furthermore found processes for the preparation of the compounds and methods for controlling undesirable plant growth with these novel compounds.

The compounds I are obtained, for example, by etherifying an appropriately substituted 5-hydroxymethylisoxazoline derivative II with a compound III in a conventional manner in an inert organic solvent in the presence of a base to give an isoxazoline I.



II III I

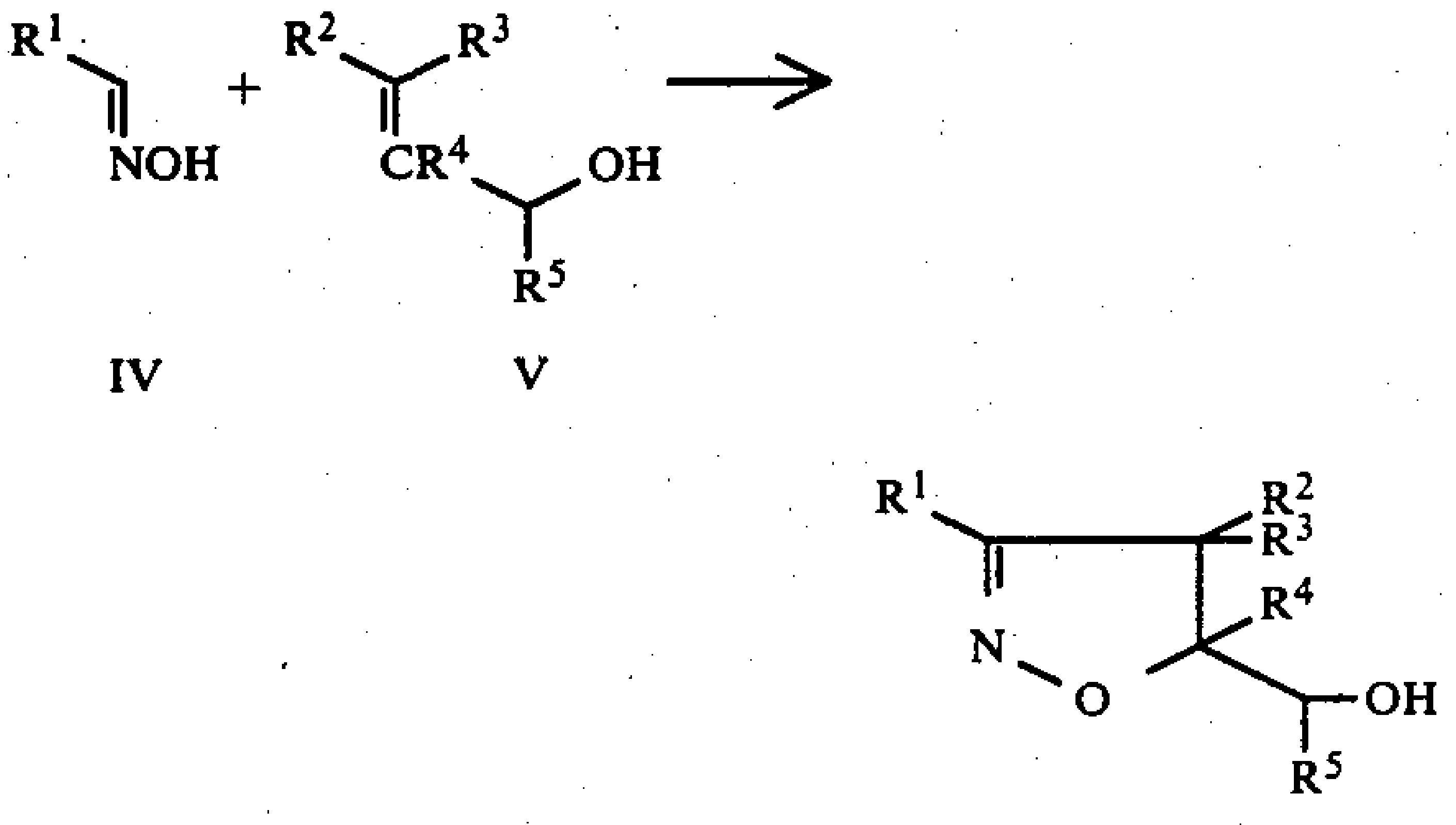
In formula III, Nu is a nucleophilic leaving group, such as chlorine, bromine, iodine, arylsulfonyl or alkylsulfonyl, e.g. toluenesulfonyl, or another equivalent leaving group. Compounds of the formula III having a reactive substituent Nu are known from the literature or are readily obtainable on the basis of the general technical knowledge.

This reaction is generally carried out at from 0° to 120° C., preferably from 10° to 80° C., in an aprotic solvent, preferably in an ether, such as diethyl ether, methyl tert-butyl ether, tetrahydrofuran or dioxane, or dimethyl sulfoxide, dimethylformamide or a mixture of these.

Examples of suitable bases are alkali metal or alkaline earth metal hydrides, such as NaH or CaH_2, alkali metal hydroxides, such as NaOH or KOH, alkali metal carbonates, such as Na_2CO_3 or K_2CO_3, alkali metal amides, such as sodium amide or lithium diisopropylamide, and tertiary amines, such as triethylamine, diisopropylethylamine, N,N-dimethyl-p-aminopyridine, N-methylpyrrolidine, N,N,N',N'-tetramethylethylenediamine, 1,5-diazabicyclo[4.3.0]non-5-ene and 1,8-diazabicyclo[5.4.0]undec-7-ene. The reaction is preferably carried out in the presence of one of the abovementioned inorganic bases.

The reaction can be accelerated by adding a phase-transfer catalyst, such as a crown ether or a quaternary ammonium salt, if heat-sensitive radicals of the educts necessitate mild reaction conditions.

The 5-hydroxymethylisoxazoline derivatives II required for the reaction are obtained in a conventional manner (C. Grundmann, Synthesis 1970, 347 and J. M. J. Trochet, S. Jaccard-Thorndahl, L. Faivre and R. Massard, Helv. Chim. Acta 56 (1973), 1303) from the corresponding oximes IV by reaction with an alkyl alcohol of the formula V,



IV V II

With regard to the use of the novel isoxazolines I in accordance with regulations, preferred substituents are the following radicals: R^1 is alkyl, such as methyl, isopropyl, n-butyl, isobutyl, tert-butyl, pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, 2,2-dimethylpropyl, 1-ethylpropyl, hexyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 4-methylpentyl, 1,1-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 2,2dimethylbutyl, 2,3-dimethylbutyl, 3,3-dimethylbutyl, 1-ethylbutyl, 2-ethylbutyl, 1,1,2-trimethylpropyl, 1,2,2trimethylpropyl, 1-ethyl-1-methylpropyl and 1-ethyl-2methylpropyl, in particular methyl, ethyl, propyl, 1-methylethyl, butyl, 1-methylpropyl, 2-methylropyl and 1,1-dimethylethyl; cycloalkyl, such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl and cycloheptyl, in particular cyclopropyl, cyclopentyl and cyclohexyl; phenyl which may be substituted by one to five, in particular one to three, halogen atoms, such as fluorine, chlorine, bromine and/or iodine, in particular fluorine, chlorine or bromine, and/or by one to three of the abovementioned C_1–C_4-alkyl groups, in particular methyl and ethyl, alkoxy groups, such as methoxy, ethoxy, propoxy, 1-methylethoxy, butoxy, 1-methylpropoxy, 2-methylpropoxy or 1,1-dimethylethoxy, in particular methoxy or ethoxy, and/or haloalkyl groups, such as fluoromethyl, difluoromethyl, trifluoromethyl, chlorodifluoromethyl, dichlorofluoromethyl, trichloromethyl, 1-fluoroethyl, 2-fluoroethyl, 2,2-difluoroethyl, 2,2,2-trifluoroethyl,2-chloro-2,2-difluoroethyl,2,2-dichloro-2-fluoroethyl, 2,2,2-trichloroethyl or pentafluoroeethyl, in particular difluoromethyl or trifluoromethyl; a saturated or unsatured 5-membered or 6-membered heterocyclic structure, such as tetrahydrofuranyl, tetrahydrothiophenyl, pyrrolidinyl, tetrahydropyranyl, tetrahydrothiopyranyl, piperidyl, furanyl, thienyl, pyrrolyl or pyridyl, in particular tetrahydropyranyl, furyl, thienyl, pyridyl or tetrahydrofuranyl; $R^2$is benzyl or C_1–C_4-alkyl as stated under R^1, in particular hydrogen, methyl or ethyl; R^3 is in general and in particular one of the radicals stated under R^2; R^4 is in general one of the radicals stated under R^2, in particular hydrogen, methyl, ethyl, propyl, 1-methylethyl or benzyl; R^5 and R^6 are each in general and in particular one of the radicals stated under R^2; and R^7 is alkenyl, such as ethenyl, 1-propenyl, 2-propenyl, 1-methylethenyl, 1-butenyl, 2-butenyl, 3butenyl, 1-methyl-1-propenyl, 1-methyl-2-propenyl, 2- methyl-1-propenyl, 2-methyl-2-propenyl, 1-pentenyl, 2-pentenyl, 3-pentenyl, 4-pentenyl, 1-methyl-1-butenyl, 2-methyl-1-butenyl,3-methyl-1-butenyl,1-methyl-2-butenyl, 2-methyl-2-butenyl, 3-methyl-2-butenyl, 1-methyl-3-butenyl, 2-methyl-3-butenyl, 3-methyl-3-butenyl, 1,1-dimethyl-2-propenyl,1-dimethyl-1-propenyl,1,-dimethyl-2-propenyl 1-dimethyl-1-propenyl,1,2-dimethyl-2-propenyl, 1-ethyl-1-propenyl, 1-ethyl-2-propenyl, 1hexenyl, 2-hexenyl, 3-hexenyl, 4-hexenyl, 5-hexenyl, 1-methyl-1-pentenyl, 2-methyl-1-pentenyl, 3-methyl-1-pentenyl, 4-methyl-1-pentenyl, 1-methyl-2-pentenyl,. 2-methyl-2-pentenyl, 3-methyl-2-pentenyl, 4-methyl-2pentenyl, 1-methyl-3-pentenyl, 2-methyl-3-pentenyl, 3-methyl-3-pentenyl, 4-methyl-3-pentenyl, 1-methyl-4-pentyl, 2-methyl-4-pentenyl, 3-methyl-4-pentenyl, 4-methyl-4-pentenyl, 1,1-dimethyl-2-butenyl, 1,1-dimethyl-3-butenyl, 1,2-dimethyl-1-butenyl, 1,2-dimethyl-2-butenyl, 1,2-dimethyl-3-butenyl, 1,3-dimethyl-1-butenyl, 1,3-dimethyl-2-butenyl, 1,3-dimethyl-3-butenyl, 2,2- dimethyl-3-butenyl,2,3-dimethyl-1-butenyl,2,3-dimethyl-2-butenyl, 2,3-dimethyl-3-butenyl, 3,3-dimethyl-1-butenyl, 1-ethyl-1-butenyl, 1-ethyl-2-butenyl, 1-ethyl-3-butenyl, 2-ethyl-1-butenyl, 2-ethyl-2-butenyl, 2-ethyl-3-butenyl, 1,2,2-trimethyl-2-propenyl, 1-ethyl-1-methyl-2-propenyl, 1-ethyl2-methyl-1-propenyl or 1-ethyl-2-methyl-2-propenyl, in particular ethenyl, 1-methylethyenyl, 2-methyl-1-propenyl or 2-methyl-1-butenyl; C_5–C_7-cycloalkenyl, such as cyclopentenyl, cyclohexenyl or cycloheptenyl, in particular cyclopentenyl or cyclohexenyl; or phenyl, naphthyl or thienyl, and when R^7 is alkenyl or cycloalkenyl it can be substituted by, in particular, phenyl and/or one to three of the halogen atoms stated under R^1, when R^7 is phenyl it can be substituted by one to three of the abovementioned halogen atoms, C_1–C_4-haloalkyl groups and/or a phenyl radical, a phenoxy radical and/or cyano groups, and when R^7 is naphthyl or thienyl it can be substituted by one to three of the abovementioned C_1–C_4-alkyl groups and/or halogen atoms.

Particularly preferred compounds I are those in which R^1 is straight-chain or branched C_1–C_5-alkyl, C_3–C_6-cycloalkyl, tetrahydropyranyl, pyridyl, furyl, phenyl, chlorophenyl, methoxyphenyl or methylphenyl, R^2 and R^3 are each hydrogen, methyl or ethyl, R^4 is hydrogen, straight-chain or branched C_1–C_4-alkyl or benzyl, R^5 and R^6 are each hydrogen or methyl and R^7 is phenyl, mono-, di- or trichlorophenyl, mono-, di- or trifluorophenyl, mono-, di-or trimethylphenyl, fluorochlorophenyl, 2-fluoro-6methylphenyl, 2,4-difluoro-6-methylphenyl, 2-chloro-6methylphenyl, bromophenyl, mono- or diethylphenyl, phenoxyphenyl, methoxyphenyl, cyanophenyl, trifluoromethylphenyl, naphthyl, thienyl, mono- or dichlorothienyl, methylthienyl, 1-methylethenyl, 1- and 2-methylpropenyl, chloroethenyl or chloropropenyl.

The isoxazolines I, or herbicidal agents containing them, may be applied for instance in the form of directly sprayable solutions, powders, suspensions (including high-percentage aqueous, oily or other suspensions), dispersions, emulsions, oil dispersions, pastes, dusts, broadcasting agents, or granules by spraying, atomizing, dusting, broadcasting or watering. The forms of application depend entirely on the purpose for which the agents are being used, but they must ensure as fine a distribution of the active ingredients according to the invention as possible.

For the preparation of solutions, emulsions, pastes and oil dispersions to be sprayed direct, mineral oil fractions of medium to high boiling point, such as kerosene or diesel oil, further coal-tar oils, and oils of vegetable or animal origin, aliphatic, cyclic and aromatic hydrocarbons such as benzene, toluene, xylene, paraffin, tetrahydronaphthalene, alkylated naphthalenes and their derivatives such as methanol, ethanol, propanol, butanol, chloroform, carbon tetrachloride, cyclohexanol, cyclohexanone, chlorobenzene, isophorone, etc., and strongly polar solvents such as dimethylformamide, dimethyl sulfoxide, N-methylpyrrolidone, water, etc. are suitable.

Aqueous formulations may be prepared from emulsion concentrates, pastes, oil dispersions or wettable powders by adding water. To prepare emulsions, pastes and oil dispersions the ingredients as such or dissolved in an oil or solvent may be homogenized in water by means of wetting or dispersing agents, adherents or emulsifiers. Concentrates which are suitable for dilution with water may be prepared from active ingredient, wetting agent, adherent, emulsifying or dispersing agent and possibly solvent or oil.

Examples of surfactants are: alkali metal, alkaline earth metal and ammonium salts of ligninsulfonic acid, naphthalenesulfonic acids, phenolsulfonic acids, alkylaryl sulfonates, alkyl sulfates, and alkyl sulfonates, alkali metal and alkaline earth metal salts of dibutylnaphthalenesulfonic acid, lauryl ether sulfate, fatty alcohol sulfates, alkali metal and alkaline earth metal salts of fatty acids, salts of sulfated hexadecanols, heptadecanols, and octadecanols, salts of sulfated fatty alcohol glycol ethers, condensation products of sulfonated naphthalene and naphthalene derivatives with formaldehyde, condensation products of naphthalene or naphthalenesulfonic acids with phenol and formaldehyde, polyoxyethylene octylphenol ethers, ethoxylated isooctylphenol ethoxylated octylphenol and ethoxylated nonylphenol, alkylphenol polyglycol ethers, tributylphenyl polyglycol ethers, alkylaryl polyether alcohols, isotridecyl alcohol, fatty alcohol ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers, ethoxylated polyoxypropylene, lauryl alcohol polyglycol ether acetal, sorbitol esters, lignin, sulfite waste liquors and methyl cellulose.

Powders, dusts and broadcasting agents may be prepared by mixing or grinding the active ingredients with a solid carrier.

Granules, e.g., coated, impregnated or homogeneous granules, may be prepared by bonding the active ingredients to solid carriers. Examples of solid carriers are mineral earths such as silicic acid, silica gels, silicates, talc, kaolin, attapulgus clay, limestone, lime, chalk, bole, loess, clay, dolomite, diatomaceous earth, calcium sulfate, magnesium sulfate, magnesium oxide, ground plastics, fertilizers such as ammonium sulfate, ammonium phosphate, ammonium nitrate, and ureas, and vegetable products such as grain flours, bark meal, wood meal, and nutshell meal, cellulosic powders, etc.

The formulations contain from 0.1 to 95, and preferably 0.5 to 90, % by weight of active ingredients.

Examples of formulations are given below.

I. 90 parts by weight of compound no. 1 is mixed with 10 parts by weight of N-methyl-alpha-pyrrolidone. A mixture is obtained which is suitable for application in the form of very fine drops.

II. 20 parts by weight of compound no. 10 is dissolved in a mixture consisting of 80 parts by weight of xylene, 10 parts by weight of the adduct of 8 to 10 moles of ethylene oxide and 1 mole of oleic acid-N-monoethanolamide, 5 parts by weight of the calcium salt of dodecylbenzenesulfonic acid, and 5 parts by weight of the adduct of 40 moles of ethylene oxide and 1 mole of castor oil. By pouring the solution into 100,000 parts by weight of water and uniformly distributing it therein, an aqueous dispersion is obtained containing 0.02% by weight of the active ingredient.

III. 20 parts by weight of compound no. 17 is dissolved in a mixture consisting of 40 parts by weight of cyclohexanone, 30 parts by weight of isobutanol, 20 parts by weight of the adduct of 7 moles of ethylene oxide and 1 mole of isooctylphenol, and 10 parts by weight of the adduct of 40 moles of ethylene oxide and 1 mole of castor oil. By pouring the solution into 100,000 parts by weight of water and finely distributing it therein, an aqueous dispersion is obtained containing 0.2% by weight of the active ingredient.

IV. 20 parts by weight of compound no. 29 is dissolved in a mixture consisting of 25 parts by weight of cyclohexanol, 65 parts by weight of a mineral oil fraction having a boiling point between 210° and 280° C., and 10 parts by weight of the adduct of 40 moles of ethylene oxide and 1 mole of castor oil. By pouring the solution into 100,000 parts by weight of water and uniformly distributing it therein, an aqueous dispersion is obtained containing 0.02% by weight of the active ingredient.

V. 20 parts by weight of compound no. 50 is well mixed with 3 parts by weight of the sodium salt of diisobutylnaphthalene-alpha-sulfonic acid, 17 parts by weight of the sodium salt of a lignin-sulfonic acid obtained from a sulfite waste liquor, and 60 parts by weight of powdered silica gel, and triturated in a hammer mill. By uniformly distributing the mixture in 20,000 parts by weight of water, a spray liquor is obtained containing 0.1% by weight of the active ingredient.

VI. 3 parts by weight of compound no. 72 is intimately mixed with 97 parts by weight of particulate kaolin. A dust is obtained containing 3% by weight of the active ingredient.

VII. 30 parts by weight of compound no. 121 is intimately mixed with a mixture consisting of 92 parts by weight of powdered silica gel and 8 parts by weight of paraffin oil which has been sprayed onto the surface of this silica gel. A formulation of the active ingredient is obtained having good adherence.

VIII. 20 parts of compound no. 125 is intimately mixed with 2 parts of the calcium salts of dodecylbenzenesulfonic acid, 8 parts of a fatty alcohol polyglycol ether, 2 parts of the sodium salt of a phenolsulfonic acid-urea-formaldehyde condensate and 68 parts of a paraffinic mineral oil. A stable oily dispersion is obtained.

The active ingredients may be applied pre- or post-emergence. If certain crop plants tolerate the active ingredients less well, application techniques may be used in which the herbicidal agents are sprayed from suitable equipment in such a manner that the leaves of sensitive crop plants are if possible not touched, and the agents reach the soil or the unwanted plants growing beneath the crop plants (post-directed, lay-by treatment).

The application rates depend on the objective to be achieved, the time of the year, the plants to be combated and their growth stage, and are from 0.001 to 3.0, preferably 0.01 to 1.0, kg of active ingredient per hectare.

In view of the number of application methods possible, the compounds according to the invention, or agents containing them, may be used in a further large number of crops for removing unwanted plants. The following crops are given by way of example:

Botanical name	Common name
Allium cepa	onions
Ananas comosus	pineapples
Arachis hypogaea	peanuts (groundnuts)
Asparagus officinalis	asparagus
Avena sativa	oats
Beta vulgaris spp. *altissima*	sugarbeets
Beta vulgaris spp. *rapa*	fodder beets
Beta vulgaris spp. *esculenta*	table beets, red beets
Brassica napus var. *napus*	rapeseed
Brassica napus var. *napobrassica*	swedes
Brassica napus var. *rapa*	turnips
Brassica rapa var. *silvestris*	
Camellia sinensis	tea plants
Carthamus tinctorius	safflower
Carya illinoinensis	pecan trees
Citrus limon	lemons
Citrus maxima	grapefruits
Citrus reticulata	mandarins
Citrus sinensis	orange trees
Coffea arabica (*Coffea canephora, Coffea liberica*)	coffee plants
Cucumis melo	melons
Cucumis sativus	cucumbers
Cynodon dactylon	Bermudagrass
Daucus carota	carrots
Elais guineensis	oil palms
Fragaria vesca	strawberries
Glycine max	soybeans
Gossypium hirsutum (*Gossypium arboreum, Gossypium herbaceum, Gossypium vitifolium*)	cotton
Helianthus annuus	sunflowers
Helianthus tuberosus	Jerusalem artichoke
Hevea brasiliensis	rubber plants

-continued

Botanical name	Common name
Hordeum vulgare	barley
Humulus lupulus	hops
Ipomoea batatas	sweet potatoes
Juglans regia	walnut trees
Lactuca sativa	lettuce
Lens culinaris	lentils
Linum usitatissimum	flax
Lycopersicon lycopersicum	tomatoes
Malus spp.	apple trees
Manihot esculenta	cassava
Medicago sativa	alfalfa (lucerne)
Mentha piperita	peppermint
Musa spp.	banana plants
Nicotiana tabacum (*N. rustica*)	tobacco
Olea europaea	olive trees
Oryza sativa	rice
Panicum miliaceum	millet
Phaseolus lunatus	limabeans
Phaseolus mungo	mungbeans
Phaseolus vulgaris	snapbeans, green beans, dry beans
Pennisetum glaucum	pearl millet
Petroselinum crispum spp. *tuberosum*	parsley
Picea abies	Norway spruce
Abies alba	fir trees
Pinus spp.	pine trees
Pisum sativum	English peas
Prunus avium	cherry trees
Prunus domestica	plum trees
Prunus dulcis	almond trees
Prunus persica	peach trees
Pyrus communis	pear trees
Ribes sylvestre	redcurrants
Ribes uva-crispa	gooseberries
Ricinus communis	castor-oil plants
Saccharum officinarum	sugar cane
Secale cereale	rye
Sesamum indicum	sesame
Solanum tuberosum	Irish potatoes
Sorghum bicolor (*s. vulgare*)	sorghum
Sorghum dochna	sorgo
Spinacia oleracea	spinach
Theobroma cacao	cacao plants
Trifolium pratense	red clover
Triticum aestivum	wheat
Triticum durum	durum wheat
Vaccinium corymbosum	blueberries
Vaccinium vitis-idaea	cranberries
Vicia faba	tick beans
Vigna sinensis (*V. unguiculata*)	cow peas
Vitis vinifera	grapes
Zea mays	Indian corn, sweet corn, maize

To increase the spectrum of action and to achieve synergistic effects, the isoxazolines of the formula I may be mixed and applied together with numerous representatives of other herbicidal or growth-regulating active ingredients groups. Examples of suitable components are diazines, 4H-3,1-benzoxazine derivative, benzothiadiazinones, 2,6-dinitroanilines, N-phenylcarbamates, thiolcarbamates, halocarboxylic acids, triazines, amides, ureas, diphenyl ethers, triazinones, uracils, benzofuran derivatives, cyclohexane-1,3-dione derivatives, quinolinecarboxylic acid derivatives, phenyloxy- or heteroaryloxy-phenylpropionic acids and salts, esters and amides thereof, etc.

It may also be useful to apply the novel compounds of the formula I, either alone or in combination with other herbicides, in admixture with other crop protection agents, e.g., agents for combating pests or phytopathogenic fungi or bacteria. The compounds may also be mixed with solutions of mineral salts used to remedy nutritional or trace element deficiencies. Non-phytotoxic oils and oil concentrates may also be added.

SYNTHESIS EXAMPLES

The directions given in the synthesis examples below were employed, after appropriate modifications to the starting materials, to obtain further compounds of the formula I; the compounds obtained are listed in the tables below with physical data. Those compounds for which no data are given may be produced analogously from the appropriate materials. In view of their close structural similarity with the compounds produced and investigated, they are expected to have a similar action.

EXAMPLE 1

Manufacturing example for a starting material of the formula II: 5-hydroxymethyl-5-methyl-3-phenyl-4,5-dihydro-1,2-oxazole

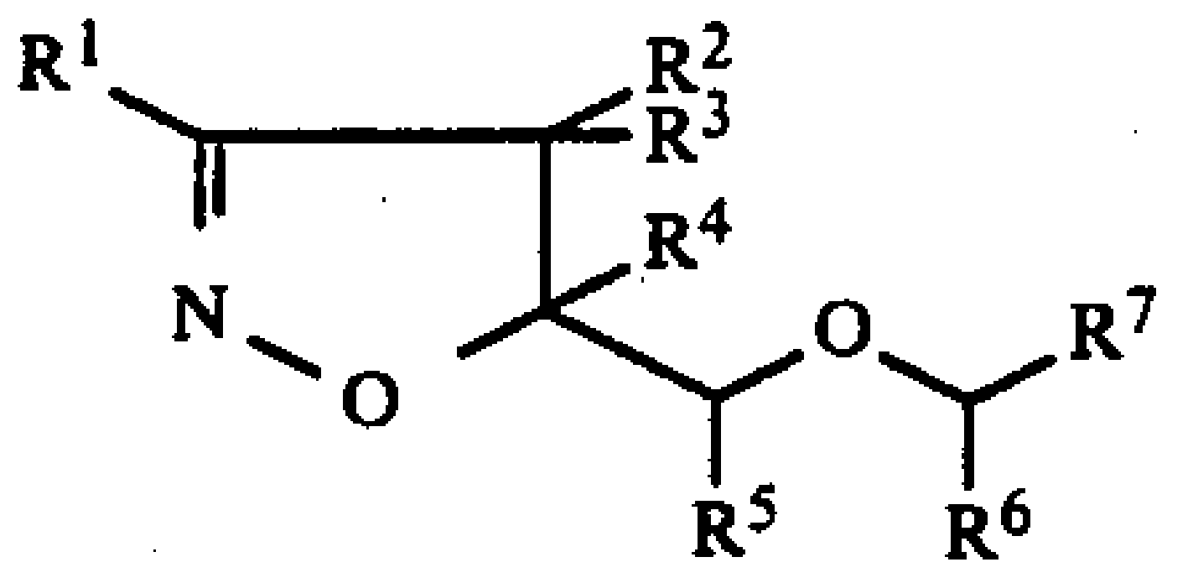
At 10° C., 380 g of a 10% strength sodium hypochloride solution in which 0.3 g of sodium hydroxide is additionally dissolved is added dropwise to 50.0 g of benzaldoxime and 37.2 g of 2-methyl-2-propenol in 80 ml of diethyl ether. The mixture is stirred overnight at room temperature, the organic phase is separated off and extracted 5 times, each time with 100 ml of diethyl ether, and the extracts are dried over sodium sulfate and evaporated down. There remains 72.3 g of crude product, which is distilled at 140° C./0.01 mbar. Melting point: 49°-50° C. Further 4,5-dihydro-1,2-oxazoles may be prepared analogously.

EXAMPLE 2

General manufacturing example for isoxazolines of the formula I:

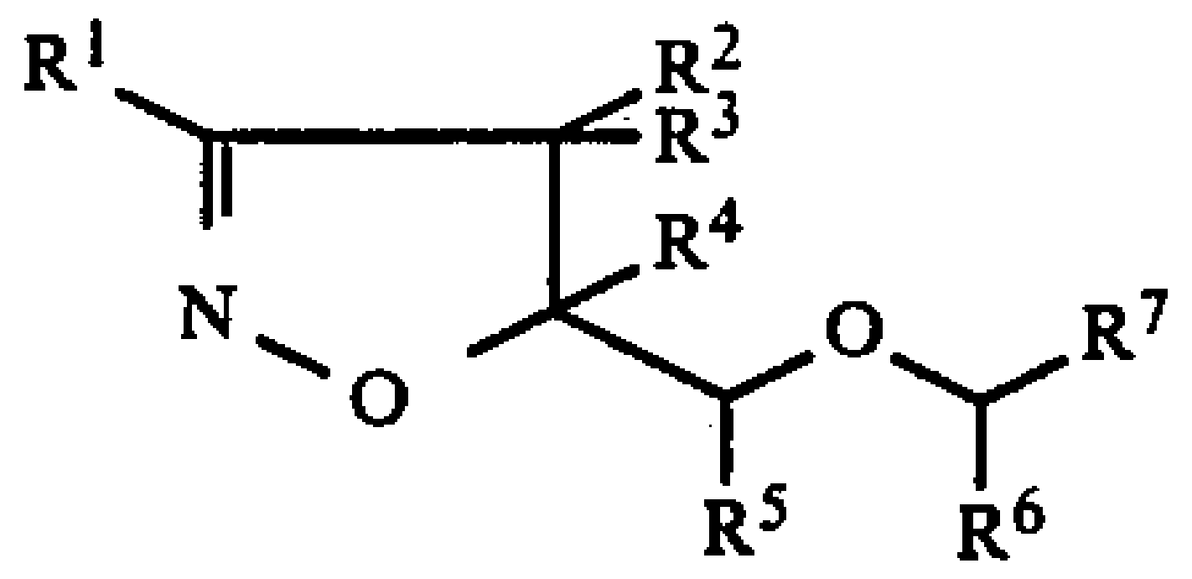
0.12 mol of sodium hydride is added to 50 ml of a 1:1 mixture of tetrahydrofuran and dimethylformamide. At room temperature, a solution of 0.10 ml of a 5-hydroxymethyl-4,5-dihydro-1,2-oxazole in 80 ml of a 1:1 mixture of tetrahydrofuran and dimethylformamide is then dripped in and the mixture is stirred for 1 hour at 60° C. Subsequently, a solution of 0.1 mol of the particular benzyl or allyl halide in 20 ml of the same solvent mixture is dripped in at room temperature. In many cases, the mixture has to be stirred for a further 2 hours at 60° C. to complete the conversion. The mixture is then stirred into 1 liter of ice water, extracted, dried and evaporated down. The crude product may be purified further by chromatography over silica gel or distillation under reduced pressure.

TABLE



No.	R^1	R^2	R^3	R^4	R^5	R^6	R^7	Phys. data
1	methyl	H	H	CH_3	H	H	phenyl	
2	methyl	H	H	CH_3	H	H	2-methylphenyl	
3	methyl	H	H	CH_3	H	H	2-fluorophenyl	
4	ethyl	H	H	CH_3	H	H	phenyl	
5	ethyl	H	H	CH_3	H	H	2-methylphenyl	^1H: 1.13(t), 1.38(s), 2.20–2.40 (m), 2,35(s)
6	ethyl	H	H	CH_3	H	H	2-chlorophenyl	
7	ethyl	H	H	CH_3	H	H	2-chloro-6-fluorophenyl	n_D^{24} = 1.5102
8	ethyl	H	H	CH_3	H	H	2-fluorophenyl	
9	isopropyl	H	H	CH_3	H	H	phenyl	
10	isopropyl	H	H	CH_3	H	H	2-chlorophenyl	
11	isopropyl	H	H	CH_3	H	H	2-fluorophenyl	^1H: 1.10(d), 1.37(s), 2.60(d), 3.00(d), 4.55(s)
12	isopropyl	H	H	CH_3	H	H	2-chloro-6-fluorophenyl	n_D^{23} = 1.5058
13	isopropyl	H	H	CH_3	H	H	3-phenoxyphenyl	n_D^{23} = 1.5425
14	isopropyl	H	H	CH_3	H	H	2-cyanophenyl	n_D^{23} = 1.5214
15	isopropyl	H	H	CH_3	H	H	2-methoxyphenyl	n_D^{24} = 1.5106
16	isopropyl	H	H	CH_3	H	H	2-trifluoromethylphenyl	n_D^{23} = 1.4731
17	isopropyl	H	H	CH_3	H	H	2,4-difluorophenyl	n_D^{24} = 1.4854
18	isopropyl	H	H	CH_3	H	H	1-naphthyl	n_D^{23} = 1.5594
19	isopropyl	H	H	CH_3	H	H	2,4,6-trimethylphenyl	n_D^{23} = 1.5035
20	isopropyl	H	H	CH_3	H	H	2-thienyl	n_D^{22} = 1.5145
21	isopropyl	H	H	CH_3	H	H	3-chloro-2-thienyl	
22	isopropyl	H	H	CH_3	H	H	2-chloro-4-thienyl	
23	isopropyl	H	H	CH_3	H	H	1-methylethenyl	n_D^{24} = 1.4554
24	isopropyl	H	H	CH_3	H	H	2-methylpropen-1-yl	n_D^{23} = 1.4604
25	isopropyl	H	H	CH_3	H	H	2-chloropropen-1-yl	
26	1-methylpropyl	H	H	CH_3	H	H	phenyl	
27	1-methylpropyl	H	H	CH_3	H	H	2-chlorophenyl	
28	1-methylpropyl	H	H	CH_3	H	H	2-fluorophenyl	
29	1-methylpropyl	H	H	CH_3	H	H	2-methylphenyl	^1H: 0.80–1.00(m), 1.43(s), 3.40–3.55(m), 4.57(cm).
30	1-methylpropyl	H	H	CH_3	H	H	2-chloro-6-fluorophenyl	n_D^{24} = 1.5030
31	1-methylpropyl	H	H	CH_3	H	H	2,4-difluorophenyl	
32	2-methylpropyl	H	H	CH_3	H	H	phenyl	
33	2-methylpropyl	H	H	CH_3	H	H	2-methylphenyl	n_D^{24} = 1.5023
34	2-methylpropyl	H	H	CH_3	H	H	2-chlorophenyl	
35	2-methylpropyl	H	H	CH_3	H	H	2-fluorophenyl	
36	2-methylpropyl	H	H	CH_3	H	H	2-chloro-6-fluorophenyl	n_D^{24} = 1.5031
37	cyclopropyl	H	H	CH_3	H	H	phenyl	
38	cyclopropyl	H	H	CH_3	H	H	2-methylphenyl	n_D^{23} = 1.9256
39	cyclopropyl	H	H	CH_3	H	H	2-chlorophenyl	
40	cyclopropyl	H	H	CH_3	H	H	2-fluorophenyl	
41	cyclopropyl	H	H	CH_3	H	H	2,4-difluorophenyl	
42	cyclopropyl	H	H	CH_3	H	H	2-chloro-6-fluorophenyl	n_D^{23} = 1.5231
43	cyclopentyl	H	H	CH_3	H	H	phenyl	
44	cyclopentyl	H	H	CH_3	H	H	2-methylphenyl	n_D^{24} = 1.5232
45	cyclopentyl	H	H	CH_3	H	H	2-chlorophenyl	
46	cyclopentyl	H	H	CH_3	H	H	2-fluorophenyl	
47	cyclopentyl	H	H	CH_3	H	H	2-chloro-6-fluorophenyl	n_D^{24} = 1.5210
48	cyclopentyl	H	H	CH_3	H	H	2,4-difluorophenyl	
49	phenyl	H	H	CH_3	H	H	phenyl	
50	phenyl	H	H	CH_3	H	H	2-methylphenyl	n_D^{24} = 1.5710
51	phenyl	H	H	CH_3	H	H	2-chlorophenyl	
52	phenyl	H	H	CH_3	H	H	2-chloro-6-fluorophenyl	^1H: 1.47(s), 2.95(d), 3.45(d) 4.75 (s)
53	phenyl	H	H	CH_3	H	H	2-fluorophenyl	
54	4-tetrahydropyranyl	H	H	CH_3	H	H	phenyl	
55	4-tetrahydropyranyl	H	H	CH_3	H	H	2-methylphenyl	n_D^{23} = 1.5246
56	4-tetrahydropyranyl	H	H	CH_3	H	H	2-chlorophenyl	
57	4-tetrahydropyranyl	H	H	CH_3	H	H	2-fluorophenyl	
58	4-tetrahydropyranyl	H	H	CH_3	H	H	2-chloro-6-fluorophenyl	n_D^{23} = 1.5236
59	3-tetrahydropyranyl	H	H	CH_3	H	H	2-methylphenyl	n_D^{23} = 1.5234
60	methyl	H	H	H	CH_3	H	2-chloro-6-fluorophenyl	$bp._{0.4}$ = 158–160
61	methyl	H	H	H	CH_3	H	2,6-dichlorophenyl	$bp._{0.2}$ = 158–160
62	methyl	H	H	H	CH_3	H	2-chlorophenyl	$bp._{0.3}$ = 150–152
63	ethyl	H	H	H	H	H	4-chloro-2-fluorophenyl	$bp._{0.4}$ = 163–165
64	ethyl	H	H	H	H	H	2,3,6-trichlorophenyl	$bp._{0.3}$ = 208–210
65	ethyl	H	H	H	H	H	2-chlorophenyl	$bp._{0.3}$ = 158–160
66	ethyl	H	H	H	H	H	2,6-dichlorophenyl	$bp._{0.2}$ = 183–185
67	ethyl	H	H	H	H	H	2-chloro-6-fluorophenyl	$bp._{0.2}$ = 157–158
68	ethyl	H	H	H	H	H	phenyl	$bp._{0.4}$ = 148–150
69	ethyl	H	H	H	H	H	2-methylphenyl	$bp._{0.4}$ = 162–164

TABLE-continued



No.	R^1	R^2	R^3	R^4	R^5	R^6	R^7	Phys. data
70	methyl	H	H	H	H	H	phenyl	bp.$_{0.1}$ = 126–128
71	methyl	H	H	H	H	H	2-methylphenyl	bp.$_{0.06}$ = 146–148
72	methyl	H	H	H	H	H	2-chloro-6-fluorophenyl	bp.$_{0.05}$ = 166–168
73	methyl	H	H	H	H	H	2,6-dichlorophenyl	bp.$_{2}$ = 192–194
74	methyl	H	H	H	H	H	2-chlorophenyl	bp.$_{0.05}$ = 156–158
75	methyl	H	H	H	H	H	4-chloro-2-fluorophenyl	bp.$_{0.3}$ = 156–158
76	methyl	H	H	H	H	H	2,3,6-trichlorophenyl	bp.$_{0.5}$ = 208–210
77	methyl	H	H	H	H	H	2-chloro-4-flourophenyl	bp.$_{0.06}$ = 160–162
78	methyl	H	H	H	H	H	4-fluorophenyl	bp.$_{0.05}$ = 144–146
79	methyl	H	H	H	H	H	2,4-dichlorophenyl	bp.$_{0.4}$ = 172–174
80	methyl	H	H	H	H	H	3,4-dichlorophenyl	bp.$_{1.2}$ = 184–187
81	isopropyl	H	H	CH_3	H	H	2,6-difluorophenyl	n_D^{23} = 1.4848
82	isopropyl	H	H	CH_3	H	H	2,6-dimethylphenyl	n_D^{23} = 1.5075
83	1-methylpropyl	H	H	CH_3	H	H	3-chloro-2-thienyl	n_D^{24} = 1.5045
84	1-methylpropyl	H	H	CH_3	H	H	2-chloro-4-thienyl	n_D^{24} = 1.5240
85	1-methylpropyl	H	H	CH_3	H	H	2-trifluoromethylphenyl	n_D^{24} = 1.4716
86	3-tetrahydropyranyl	H	H	CH_3	H	H	2-chloro-6-fluorophenyl	n_D^{23} = 1.5212
87	3-tetrahydropyranyl	H	H	CH_3	H	H	2-fluorophenyl	
88	n-propyl	H	H	CH_3	H	H	phenyl	
89	n-propyl	H	H	CH_3	H	H	2-methylphenyl	
90	n-propyl	H	H	CH_3	H	H	2-chloro-6-fluorophenyl	
91	n-propyl	H	H	CH_3	H	H	2-fluorophenyl	
92	n-propyl	H	H	CH_3	H	H	2-bromophenyl	
93	t-butyl	H	H	CH_3	H	H	2-chloro-6-fluorophenyl	n_D^{22} = 1.5010
94	t-butyl	H	H	CH_3	H	H	2-methylphenyl	n_D^{22} = 1.5020
95	t-butyl	H	H	CH_3	H	H	2-fluorophenyl	
96	t-butyl	H	H	CH_3	H	H	2-ethylphenyl	
97	t-butyl	H	CH_3	CH_3	H	H	2-methylphenyl	
98	phenyl	CH_3	CH_3	CH_3	H	H	2-methylphenyl	
99	isopropyl	H	H	ethyl	H	H	2-methylphenyl	n_D^{24} = 1.5050
100	isopropyl	H	H	ethyl	H	H	2-chloro-6-fluorophenyl	n_D^{24} = 1.5036
101	isopropyl	H	H	ethyl	H	CH_3	2-chloro-6-fluorophenyl	
102	isopropyl	H	H	benzyl	H	H	2-methylphenyl	
103	isopropyl	H	H	benzyl	H	H	2-chloro-6-fluorophenyl	n_D^{24} = 1.5420
104	isopropyl	H	H	benzyl	H	H	2-fluorophenyl	
105	isopropyl	H	H	i-propyl	H	H	2-methylphenyl	n_D^{24} = 1.5049
106	isopropyl	H	H	i-propyl	H	H	2-chloro-6-fluorophenyl	n_D^{24} = 1.5035
107	2-furyl	H	H	CH_3	H	H	2-chloro-6-fluorophenyl	
108	2-furyl	H	H	CH_3	H	H	2-methylphenyl	
109	2-thienyl	H	H	CH_3	H	H	2-methylphenyl	
110	3-pyridyl	H	H	CH_3	H	H	2-methylphenyl	
111	3-pyridyl	H	H	CH_3	H	H	2-chloro-6-fluorophenyl	
112	2-chlorophenyl	H	H	CH_3	H	H	2-methylphenyl	
113	2-chlorophenyl	H	H	CH_3	H	H	2-chloro-6-fluorophenyl	n_D^{24} = 1.5705
114	3-chlorophenyl	H	H	CH_3	H	H	2-methylphenyl	
115	4-chlorophenyl	H	H	CH_3	H	H	2-fluorophenyl	
116	2-methoxyphenyl	H	H	CH_3	H	H	2-methylphenyl	
117	2-methoxyphenyl	H	H	CH_3	H	H	2-chloro-6-fluorophenyl	
118	2-methoxyphenyl	H	H	CH_3	H	H	phenyl	
119	isopropyl	H	H	n-propyl	H	H	2-methylphenyl	
120	n-butyl	H	H	CH_3	H	H	2-chloro-6-fluorophenyl	
121	isopropyl	H	H	CH_3	H	H	2-methylphenyl	^{1}H: 1.10(d), 1.37(s), 2.30(s), 4.60(mc)
122	isopropyl	H	H	H	H	H	4-fluorophenyl	^{1}H: 1.15(d), 2.60–3.10(m), 4.55(s)
123	isopropyl	H	H	H	H	H	2-methylphenyl	^{1}H: 1.12(d), 2.32(s), 2.60–3.10(m) 3.45–3.65(m), 4.55(s) 4.60–4.80(m).
124	methyl	H	H	H	H	H	2-fluorophenyl	n_D^{24} = 1.5094
125	isopropyl	H	H	CH_3	H	CH_3	phenyl	n_D^{23} = 1.4850
126	2-chlorophenyl	H	H	CH_3	H	H	2-fluorophenyl	n_D^{25} = 1.5642
127	2-methoxyphenyl	H	H	CH_3	H	H	2-chlorophenyl	n_D^{23} = 1.5784
128	isopropyl	H	H	benzyl	H	H	phenyl	n_D^{24} = 1.5425

*refractive indexes (n_D), boiling points (Kp) in C.° or selected ^{1}H-NMR signals: δ in ppm using tetramethylsilane as internal standard (^{1}H).

USE EXAMPLES

The action of the isoxazolines of the formula I on plant growth is demonstrated by the following greenhouse experiments:

The vessels employed were plastic flowerpots having a volume of 300 cm^3 and filled with a sandy loam containing about 3.0% humus. The seeds of the test plants were sown separately, according to species.

For the preemergence treatment, the active ingredients were applied to the surface of the soil immediately after the seeds had been sown. The compounds were emulsified or suspended in water as vehicle, and sprayed through finely distributing nozzles. After the agents had been applied, the vessels were lightly sprinkler-irrigated to induce germination and growth. Transparent plastic covers were then placed on the vessels until the plants had taken root. The cover ensured uniform germination of the plants, insofar as this was not impaired by the active ingredients. The application rates were 0.5 and 1.0 kg/ha.

For the postemergence treatment, the plants were grown, depending on growth form, to a height of 3 to 15 cm before being treated. In this treatment method, either plants which had been sown in the pots and grown there were selected, or they were cultivated separately as seedlings and transplanted to the pots a few days before being treated. The application rate for postemergence treatment was 1.0 kg/ha. No covers were placed on the vessels in this method.

The pots were set up in the greenhouse, species from warmer climates in warmer areas (20° to 35° C.) and species from moderate climates at 10° to 20 ° C. The experiments were run for from 2 to 4 weeks. During this time the plants were tended and their reactions to the various treatments assessed. The assessment scale was 0 to 100, 100 denoting nonemergence or complete destruction of at least the visible plant parts, and 0 denoting no damage or normal growth.

The plants used in the greenhouse experiments were:

Abbrev.	Botanical name	Common name
BRNSW	*Brassica napus*	rapeseed
BROIN	*Bromus inermis*	smooth broome
CHEAL	*Chenopodium album*	lambsquarters (goosefoot)
ELEIN	*Eleusine indica*	
ECHCG	*Echinochloa crus-galli*	barnyardgrass
HELAN	*Helianthus annus*	sunflowers
LOLMU	*Lolium multiflorum*	annual ryegrass
POAAN	*Poa annua*	annual bluegrass

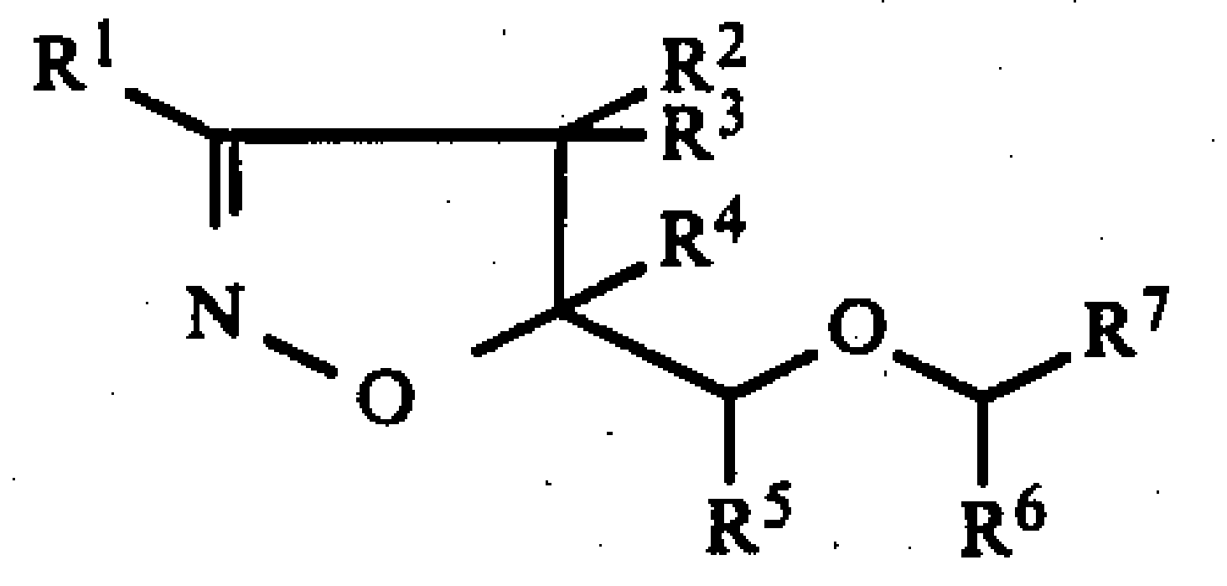
The compounds of Examples 7 and 12, applied preemergence at a rate of 1.0 kg/ha, combated unwanted plants extremely well, and were well tolerated by rape.

Compound no. 52, applied postemergence at a rate of 1.0 kg/ha, had a herbicidal action on Chenopodium album without damaging crop plants.

Compound no. 42, applied preemergence at a rate of 0.5 kg/ha, had a very good herbicidal action of broadleaved plants without damaging, for instance, sunflowers.

We claim:

1. An isoxazoline of the formula I



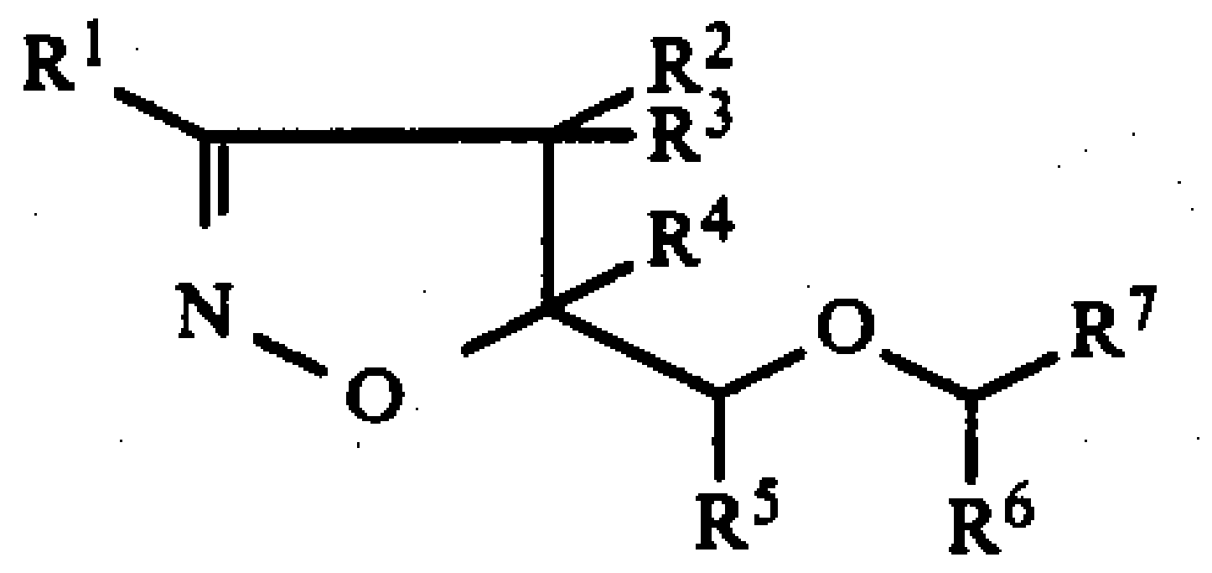
where the substituents have the following meanings:

R^1 is phenyl substituted by from one to five halogens and from one to three of the groups C_1-C_4-alkyl, C_1-C_4-alkoxy or C_1-C_4-haloalkyl; or phenyl substituted by from one to five halogens or by from one to three of the groups C_1-C_4-alkyl, C_1-C_4-alkoxy or C_1-C_4-haloalkyl

R^2, R^3, R^4, R^5 and R^6 are hydrogen, C_1-C_4-alkyl or benzyl and

R^7 is C_2-C_6-alkenyl or C_5-C_7-cycloalkenyl, or C_2-C_6-alkenyl or C_5-C_7-cycloalkenyl substituted by one to three phenyl radicals and halogen atoms, or C_2-C_6-alkenyl or C_5-C_7-cycloalkenyl substituted by one to three; phenyl radicals or halogen atoms; unsubstituted phenyl or phenyl substituted by from one to three of the following substituents: C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-haloalkyl, phenyl, phenoxy, cyano and halogen; or unsubstituted naphthyl or thienyl, or naphthyl or thienyl substituted by from one to three C_1-C_4-alkyl groups and halogen atoms, or naphthyl or thienyl substituted by from one to three C_1-C_4-alkyl groups or halogen atoms.

2. A process for combating the growth of unwanted plants, wherein the unwanted plants or their habitat are treated with a herbicidally effective amount of an isoxazoline of the formula I



where the substituents have the following meanings:

R^1 is C_1-C_{12}-alkyl, C_3-C_7-cycloalkyl, unsubstituted phenyl or phenyl substituted by from one to five halogens and from one to three of the groups C_1-C_4-alkyl, C_1-C_4-alkoxy or C_1-C_4-haloalkyl; or phenyl substituted by from one to five halogens or by from one to three of the group C_1-C_4-alkyl, C_1-C_4-alkoxy or C_1-C_4-haloalkyl; or R^1 is tetrahydrofuranyl, tetrahydrothiophenyl, pyrrolidinyl, tetrahydropyranyl, tetrahydrothiopyranyl, piperidyl, furanyl, thienyl, pyrrolyl or pyridyl directly attached to the 3-position of the isoxazoline ring;

R^2, R^3, R^4, R^5 and R^6 are hydrogen, C_1-C_4-alkyl or benzyl and

R^7 is C_2-C_6-alkenyl or C_5-C_7-cycloalkenyl, or C_2-C_6-alkenyl or C_5-C_7-cycloalkenyl substituted by one to three phenyl radicals or halogen atoms; unsubstituted phenyl or phenyl substituted by from one to three of the following substituents: C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-haloalkyl, phenyl, phenoxy, cyano and halogen; or unsubstituted naphthyl or thienyl, or naphthyl or thienyl substituted by from one to three C_1-C_4-alkyl groups and halogen atoms, or naphthyl or thienyl substituted by one to three c_1-C_4-alkyl groups or halogen atoms.

3. A herbicidal composition containing a herbicidally effective amount of the isoxazoline of the formula I in claim 2, along with an inert carrier or diluent.

* * * * *